Simulating Solvent Effects and Liquid Behavior with the Effective Fragment Potential Method

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Outline

- Effective Fragment Potential method overview (EFP1)

- Further developments:
  - EFP1/DFT
  - EFP1/MP2
  - EFP2

- Using EFP:
  - Molecular Dynamics
  - Parallel EFP code
Why should YOU care??

- Understanding the environment
  - Most processes occur in the condensed phase
  - Biological applications

- Solvation models in use:
  - Continuum
  - Discrete

- Model to reliably predict BOTH cluster AND bulk properties
Effective Fragment Potential Method (EFP)

- Effective Fragment Potential
- Discrete solvent effects

Division of system:

\[ E_{\text{system}} = E_{\text{ab initio}} + E_{\text{interaction}} \]

- EFP is much less computationally expensive!!
EFP Method

- Effect of “solvent” molecules (fragments) added as one-electron terms to *ab initio* Hamiltonian, $H_{AR}$

$$H_{system} = H_{AR} + V$$

- **FRAGMENT** potential ($V$):
  - Obtained by separate AI calculations
  - Depends on properties of isolated molecules
  - Can be systematically improved
  - Only one-electron integrals!
EFP Method

\[ V_{el}(\mu, s) = \sum_{k=1}^{K} V_k^{Elec} (\mu, s) + \sum_{l=1}^{L} V_l^{Pol} (\mu, s) + \sum_{m=1}^{M} V_m^{Re} (\mu, s) \]

- **Electrostatics**: Coulomb interactions
  - Distributed multipolar expansion up to octupoles

- **Polarization**: Dipole/induced dipole potential
  - Localized molecular orbital (LMO) polarizability expansion
  - Induced dipoles iterated to self-consistency

- **Exchange repulsion/charge transfer**: Remainder term
  - EFP1: fit to functional form
Further Developments

- **EFP1/DFT:**
  - Initial *ab initio* calculations based on DFT (versus EFP1/HF)

- **EFP1/MP2:**
  - Initial calculations based on MP2
  - Dispersion term from MP2 included

- **EFP2:** Generalize the EFP method
  - Exchange repulsion from first principles (NO FITS!)
  - Generalized dispersion term in progress
EFP Method in Use

- EFP1/HF has been shown to represent water clusters and solvation reactions well
  - Reproduce *ab initio* results

- First test of EFP to reproduce bulk behavior:
  - Implementation of EFP and Molecular Dynamics (MD) within GAMESS
Molecular Dynamics + EFP

- Solve Newton’s equations of motion to propagate a system through time
  - Use EFP to generate energy and gradients (forces)

  - Do \( i = 1 \), number of simulation steps
    - Calculate PE and gradients \( \rightarrow \) forces for particle at time \( t \)
    - Solve equations of motion for each particle to obtain KE at time \( t \) and new positions at time \( t + dt \)
  - End do

- Currently implemented:
  - EFP1/HF, EFP1/DFT, EFP1/MP2*
  - SPC/E
  - EFP2/HF* and AI MD*
**MD + EFP**

- **Integration:**
  - EFP water is a rigid molecule--center of mass motion
    - Translational motion: leapfrog algorithm
    - Rotational motion: quaternions and modified leapfrog

- **Ensembles:**
  - NVE (constant energy)
  - NVT (constant temperature)
    - Based on velocity scaling: rescale by $\sqrt{\frac{T_0}{T(t)}}$

- **Periodic boundary conditions and minimum image convention implemented for EFP-EFP MD**
MD + EFP

- Objectives:
  - Compare EFP with other water potentials and experimental results for bulk water

- Radial distribution function (RDF)
  - Gives information on how molecules pack in neighbor ‘shells’, as well as average structure
  - Can be measured spectroscopically (X-ray or neutron diffraction)
  - 3 site-site RDFs for water (gOO(r), gOH(r), gHH(r))
RDF--62 waters

Initial structure: 62 waters, 26 ps equilibration
Timestep size = 1 fs, Simulation = 5000 fs

- gOO(r)
- gHH(r)
- gOH(r)

Graphs showing radial distribution functions for different models and comparison with experimental data.
RDF--512 waters

Initial structure: 512 waters, 7.5 ps equilibration
Timestep size = 1 fs, Simulation = 5000 fs

Exp (gOO): X-ray; Sorenson et al. J. Chem. Phys. 113, 9149(2000);
Exp (gOH, gHH): Neutron Diffraction; Soper et al.
Parallel EFP: Speedup curves (energy + gradient)

“Raw” times:
512 EFP1/HF waters:
Serial (p=1)=352.2 sec
Parallel(p=14)=39.8 sec
Conclusions/Future Plans

- EFP is a viable method for solvation
- Continuation of EFP and MD development
  - Extensions such as treatment of long range forces, use of simplectic methods (versus quaternions), inclusion of more ensemble options
  - Treatment of AI-EFP MD
- Utilization of parallel EFP with MD
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